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# ICP-MS determination of tungsten and other heavy metals in contaminated environmental samples after a borate fusion

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**Objective:** An analytical method has been established to determine the contents of tungsten (W), chromium (Cr), cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), cadmium (Cd), antimony (Sb), and lead (Pb) in contaminated soil and plant samples. Undesirable wash out effects caused by tungsten, were minimised by application of silicone tubes and matrix matched solutions. **Method:** The samples were incinerated at 550°C in order to remove organic material. The subsequent milling step homogenised the sample. 1 g of the ashed sample was digested by heating it together with a borate fusion at 1000°C for 20 minutes. The hot fusion was poured into a mixture of nitric/citric acid for further dissolution. Finally inductively coupled plasma-mass spectrometry was used to determine the amount of the metals. The calibration was performed with matrix matched multi element standard solutions. The accuracy of the analytical procedure was verified by certified reference materials. **Results:** The limit of quantification (LOQ) for tungsten in soil and plant samples was 1.3 mg/kg. The long term reproducibility for tungsten was 7-9%.

## Introduction

Due to the physical properties of tungsten (high density and high melting point), it is frequently used as anti tank ammunition. The Swiss standard procedure for the determination of the total contents of heavy metals in soil samples is based on a nitric acid extraction procedure. Unfortunately this method is not qualified for the analysis of tungsten, as in nitric acid solutions passivation and precipitation of tungsten occurs. Similar reactions are known for antimony and molybdenum. For the determination of tungsten and additional heavy metals such as chromium (Cr), cobalt (Co), nickel (Ni), zinc (Zn), arsenic (As), cadmium (Cd), antimony (Sb), and lead (Pb) a borate fusion and an ICP-MS method, based on matrix matched measurements, was developed. To avoid small pieces of tungsten and to get a representative laboratory sample, the soil was heated at 550°C and homogenised by milling.

## Methods and Materials

### Sample Preparation

#### Homogenisation of Soil Samples

Approximately 1 kg of the field collected soil sample was dried at 40°C to mass constant. The dried sample was crushed by a jaw breaker. Stones, roots, wood, and big metallic parts were eliminated by passing the sample through a 2 mm sieve. 50 g of the < 2 mm fraction was heated at 550°C in a 100 mL-quartz beaker glass for 4 hours. The entire amount of ash residue was homogenised in a ball mill (agate mortar).

#### Homogenisation of Plant Samples

The collected sample was dried at 80°C. The dried sample was pulverised by a cutting mill. The homogenised sample was incinerated according to the following program:

**Table 1** Temperature program for incinerating the plant samples

30 min	200°C
360 min	200°C
300 min	380°C
360 min	380°C
hold to mass constant	520°C

### Borate Fusion

1 g of the incinerated and homogenised sample and 4 g of Spectroflux® 100B (LiBO<sub>2</sub>= 80%; Li<sub>2</sub>B<sub>2</sub>O<sub>7</sub>= 20%) delivered by Alfa Aesar (#574000) was weighted in a PE-vessel. After blending, the mixture was transferred in a Platinum-Gold crucible (Pt/Au 95/5-DPH Ti 3/9). The mixture was heated to 1000°C for 20 minutes. The hot fused liquid mixture was poured into 100 mL of a mixture of nitric/citric acid (2 mol/L/0.5 mol/L) under vigorous stirring. The more or less clear digestion solution was transferred into a 200 mL volumetric flask and filled up to the mark with water. Finally the solution was centrifuged at 3500 rpm for 10 min in PP-tubes to separate insoluble parts. In the same way an LRB (laboratory reagent blank) was prepared.

### Sample dilution

For the ICP-MS measurements all solutions were diluted 100 times with prediluted LRB.

### ICP-MS measuring

#### Equipment

- ICP-MS ELAN 6000 (Perkin Elmer, Sciex, Canada)
- ETP Dual Stage Detector (ETP; Australia)
- ICP-MS controller software version 2.3.2 (Perkin Elmer; Canada)
- Auto sampler AS 500 (CETAC; USA)
- Peristaltic pump with silicone tubes (black-black coded) which allows better rinse and washout characteristics for tungsten (Spetec, Germany)
- Micromist nebulizer P/N AR30-1-F02 (Glass Expansion, Australia)
- Jacketed cinnabar spray chamber P/N 809-0205 (regulated to 16°C) (Glass Expansion, Australia)

### Reagents

All chemicals, single- and multielement stock solutions were certified for purity and concentrations.

#### Water R > 18 MΩ

Deionised and filtered (0.2µm) water with a resistant > 18 MΩ was used.

### Nitric acid (subboiling quality)

Nitric acid (Merck # 1.00456.2500; p.a.) was purified by subboiling-distillation technique. The subboiled nitric acid was stored in PFA bottle.

### Nitric acid 2%

23 mL of subboiled nitric acid was diluted to 1000 mL with water. The diluted nitric acid was stored in a PFA bottle.

### Citric acid anhydrous (FLUKA #27488)

### Nitric acid / Citric acid mixture (2 mol/L/0.5 mol/L)

96 g of citric acid anhydrous was dissolved in 700 mL water. 140 mL of subboiled nitric acid was added and filled up to 1 L.

### Prediluted LRB

10 mL of the LRB was diluted to 1000 mL with nitric acid (2%).

### Tungsten standard 1000 mg/L (Alfa # 35770)

### Tungsten prediluted standard

5.0 mL of tungsten  $\beta=1000$  mg/L stock solution was diluted with a mixture of nitric acid and citric acid (2 mol/L/0.5 mol/L) in a volumetric flask to 50 mL. The final concentration was  $\beta(W)=100$  mg/L.

### Initial Calibration Stock Standard EPA 6020 (ICS); (Alfa Aesar # 42602)

This solution contained the elements Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Tl, V, Zn. The concentration of each element was 10 mg/L.

### Calibration

The ICP-MS was calibrated, using matrix matched multielement standard solutions.

### ICP-MS Initial Calibration Multielement Standard

A linear four point calibration standard row was prepared by dilution of a prediluted tungsten standard and an initial calibration stock standard EPA 6020.

As dilution medium a prediluted LRB was used.

**Table 2** Initial Multi Element Calibration Standards (ICAL) for soil samples [ $\mu\text{g/L}$ ]

Element	ICAL 1	ICAL 2	ICAL 3	ICAL 4
W	75	150	225	300
Ni	25	50	75	100
Co	25	50	75	100
Cu	25	50	75	100
Cr	25	50	75	100
Other elements according to EPA 6020				

Using this calibration row, a linear working range for tungsten up to 6000  $\mu\text{g/g}$ , respectively 2000  $\mu\text{g/g}$  for the other elements in incinerated soil sample is covered.

**Table 3** Initial Multi Element Calibration Standards (ICAL) for plant samples [ $\mu\text{g/L}$ ]

Element	Ical 1	Ical 2	Ical 3	Ical 4
W	7.5	15.0	22.5	30.0
Ni	2.5	5.0	7.5	10.0
Co	2.5	5.0	7.5	10.0
Cu	2.5	5.0	7.5	10.0
Cr	2.5	5.0	7.5	10.0
Other elements according to EPA 6020				

### Quality check standard solutions

According EPA 6020 an independent QC-standard solution (ICV, CCV) is required. Therefore the ICP-MS QC-Standard

Solution 20 (Alfa # 42598) and a prediluted tungsten standard was used.

As dilution medium a prediluted LRB was used.

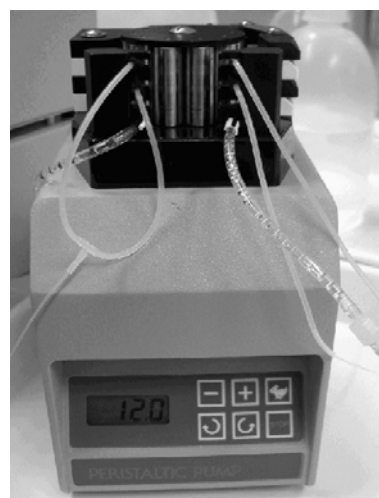
**Table 4** Quality check solutions (ICV and CCV) in [ $\mu\text{g/L}$ ]

Element	ICV (soil)	CCV (soil)	ICV (plant)	CCV (plant)
W	150	150	15.0	15.0
Ni	50	50	5.0	5.0
Co	50	50	5.0	5.0
Cu	50	50	5.0	5.0
Cr	50	50	5.0	5.0
Other elements according to EPA 6020				

### Internal Standard

Three internal standards, Indium ( $m/z=115$ ), Germanium ( $m/z=72$ ) and Terbium ( $m/z=159$ ) in concentrations of 100  $\mu\text{g/L}$  were used.

Additionally, the internal standard solution contained:  $\beta=2500$  mg/L Ca, Mg, Na, K, Fe and  $\beta=100$   $\mu\text{g/L}$   $^{209}\text{Bi}$ ,  $^6\text{Li}$ ,  $^{45}\text{Sc}$ ,  $^{89}\text{Y}$ . The matrix was nitric acid 2%. The internal Standard was added on-line to all solutions as shown in figure 1



**Fig. 1** Peristaltic pump with sample and internal standard on-line dosage.

### ICP-MS rinse solution

To rinse the system, a prediluted LRB was used.

### Selected masses

**Table 5** Internal Standards and corrections

Analyte	Mass	Istd	Corrections
In	115	<	-0.014032*Sn118
Cr	52	I	
Co	59	I	
Ni	60	I	
Cu	63	I	
Cu	65	I	
Zn	66	I	
Ge	72	<	
As	75	I	-3.127*(ArCl77-(0.815*Se82))
Cd	111	I	-1.073*(MoO108-(0.712*Pd106))
Cd	114	I	-0.026826*Sn118
In	115	<	-0.014032*Sn118
Sb	121	I	
Tl	205	I	
Pb	208	I	+1Pb206+1*Pb207
W	182	I	
W	184	I	-0.001242*Os189
Tb	159	<	

### Instrumental parameters

Table 6 shows the instrumental parameters of the ICP-MS and the isotopes used for the measurements.

**Table 6** Instrumental Parameters for the ICP-MS determination

<b>Timing Parameters</b>	
Sweeps/Reading	10
Reading per Replicates	1
Number of Replicates	6
Settling Time	Normal
Scan Mode	Peak Hopping
Dwell Time	100 ms
<b>Signal Processing</b>	
Detector Mode	Dual
Measurement Units	cps
Autolens	on
Spectral Peak Processing	Average
Signal Peak Processing	Maximum
Blank Subtraction	After Internal Standard
Baseline Readings	0
Smoothing	Yes, Factor 5
<b>Manual Settings</b>	
Plasma flow	18 L/min
Nebulizer flow	1.1 L/min
RF-power	1100 watts
<b>Liquid uptake and washout settings</b>	
Sample uptake	1.3 mL/min at 12 rpm
Sample flush	60 s
Sample flush speed	24 rpm
Read delay	60 s
Delay and analysis speed	12 rpm
Wash time	160 s
Wash speed	24 rpm

### Quality assurance

#### Calibration and stability check

To perform quality checks, an initial calibration verification standard (ICV) and a continues calibration verification standard (CCV) were used.

#### Matrix effects

In order to check for matrix effects additionally, the selected samples were diluted 500 times with prediluted LRB.

#### Limit of quantification (LOQ)

The Limit of quantification (LOQ) was determined on the basis  $10\sigma$  of the background signal for each element of the LRB-signal.

**Table 7** Limits of quantification [mg/kg] relating to incinerated sample

Element	Mass	Methodically LOQ
Cr	52	0.6
Co	59	0.02
Ni	60	0.3
Cu	63	0.5
Zn	66	2
As	75	0.05
Cd	111	0.2
Sb	121	0.05
Pb	208	0.2
W	182	1.3

#### Methodical accuracy and precision

The following tungsten certified reference materials were analysed as described above in order to check the methodical accuracy and precision especially for tungsten:

Tungsten Ore BH-1 (0.415-0.430%), Tungsten Ore TLG-1 (0.080-0.087%) (CANMET; CD), and Virginia Tobacco Leaves CTA-VTL-2 (0.233 mg W/kg) (ICHTJ; Poland).

For the additional elements IAEA/V-10 Hay (powder), BCR 279 Trace elements in Sea Lettuce, and BCR 60 Trace in an aquatic plant were used.

#### References

- 1 ASTM C 1345-96: "Standard Test Method for Analysis of Total and Isotopic Uranium and Total Thorium in Soils by ICP-MS"
- 2 EPA 6020; Inductively coupled plasma-mass spectrometry
- 3 DIN 38406 E29; 12/96: "Bestimmung von 61 Elementen durch Massenspektrometrie mit induktiv gekoppeltem Plasma"
- 4 The determination of metals (antimony, bismuth, lead, cadmium, mercury, palladium, platinum, tellurium, thallium, tin and tungsten) in urine samples by inductively coupled plasma-mass spectrometry"; P. Schramel, I. Wendler, J. Angerer; Int Arch Occup Environ Health (1997) 69:219-223; Springer-Verlag 1997
- 5 Rudolf Bock "Handbuch der analytisch-chemischen Aufschlussmethoden"; ISBN-3-527-29791-X; Wiley-VCH; P 106
- 6 Angela M. Gonzalez Ramon M. Barnes; "Comparison of microwaste assisted extraction and waste extraction test (WET) preparation for inductively coupled plasma spectroscopy analyses of waste samples"; Anal Bioanal Chem (2002) 374: 255-261
- 7 Gerald EG. Carlson, Copper Ridge Explorations Inc, Geology, mineralization and sampling results from the Kalzas tungsten property, central Yukon, Yukon Exploration and geology (2001), 269-278.
- 8 Verordnung vom 1. Juli 1998 über Belastungen des Bodens (VBBö); SR-Nummer 814.12

**Table 8** Tungsten Ore TLG-1 (0.080-0.087%) (CANMET; CD); Values in [%]; (n.c. = not certified)

Analyte	Mass	Certified	Mean	SD	RSD	Recovery	n
Cr	52	n.c.	0.0048	0.0004	9%		9
Co	59	n.c.	0.0016	0.0001	6%		9
Ni	60	n.c.	0.003	0.0002	9%		9
Cu	63	n.c.	0.032	0.002	5%		4
Zn	66	n.c.	0.022	0.001	7%		9
As	75	n.c.	0.002	0.0001	8%		9
Cd	111	n.c.	0.005	0.0003	5%		9
Sb	121	n.c.	0.0004	0.0001	29%		9
Pb	208	n.c.	0.009	0.001	6%		9
<b>W</b>	<b>182</b>	<b>0.083</b>	<b>0.080</b>	<b>0.007</b>	<b>9%</b>	<b>96%</b>	<b>9</b>

**Table 9** Tungsten Ore BH-1 (0.415-0.430%) (CANMET; CD); Values in [%]; (n.c. = not certified)

Analyte	Mass	Certified	Mean	SD	RSD	Recovery	n
Cr	52	n.c.	0.0044	0.0004	10%		9
Co	59	n.c.	0.001	0.001	85%		9
Ni	60	n.c.	0.0021	0.0003	15%		9
Cu	63	n.c.	0.0086	0.0005	5%		4
Zn	66	n.c.	0.010	0.001	9%		9
As	75	n.c.	0.037	0.003	9%		9
Cd	111	n.c.	0.0008	0.0001	18%		9
Sb	121	n.c.	0.0001	0.0000	38%		9
Pb	208	n.c.	0.020	0.001	6%		9
<b>W</b>	<b>182</b>	<b>0.422</b>	<b>0.411</b>	<b>0.028</b>	<b>7%</b>	<b>97%</b>	<b>9</b>

**Table 10** Virginia Tobacco Leaves CTA-VTL-2 (0.233 mg W/kg) (ICHTJ; Poland); Values in [mg/kg]

Analyte	Mass	Certified	Mean	SD	RSD	Recovery	n
Cr	52	1.87	2.47	0.97	39%	132%	2
Co	59	0.43	0.44	0.003	0.8%	103%	2
Ni	60	1.98	2.33	0.04	1.6%	118%	2
Cu	63	18.2	20.7	0.91	4.4%	113%	2
Zn	66	43.3	46.4	3.05	6.6%	107%	2
As	75	0.97	0.80	0.03	4.2%	82%	2
Cd	111	1.52	1.57	0.01	0.5%	103%	2
Sb	121	0.31	0.33	0.01	1.7%	107%	2
Pb	208	22.1	21.7	0.27	1.2%	98%	2
<b>W</b>	<b>182</b>	<b>0.23</b>	<b>&lt; 1.3</b>				<b>2</b>

**Table 11** IAEA/V-10 Hay (powder); Values in [mg/kg]

Analyte	Mass	Certified	Mean	SD	RSD	Recovery	n
Cr	52	6.5	7.0			107%	1
Co	59	0.13	0.17			130%	1
Ni	60	4	4.2			106%	1
Cu	63	9.4	9.5			101%	1
Zn	66	24	22.4			93%	1
Cd	111	0.03	0.04			123%	1
Pb	208	1.6	1.5			97%	1

**Table 12** BCR 279 Trace elements in Sea Lettuce; Values in [mg/kg]; (n.c. = not certified)

Analyte	Mass	Certified	Mean	SD	RSD	Recovery	n
Cr	52	11.6	12.4	0.1	0.8	107%	2
Co	59	n.c.	2.7	0.0	1.0		2
Ni	60	15.9	17.7	0.2	1.3	111%	2
Cu	63	13.14	14.5	0.6	4.2	110%	2
Zn	66	51.3	50.0	1.7	3.5	97%	2
As	75	3.09	2.1	0.2	9.2	67%	2
Cd	111	0.27	0.3	0.1	21.1	121%	2
Pb	208	13.48	11.3	0.2	1.5	84%	2

**Table 13** BCR 60 Trace in an aquatic plant; Values in [mg/kg]

Analyte	Mass	Certified	Mean	SD	RSD	Recovery	n
Cr	52	26	31.1	0.7	2.3	120%	2
Co	59	4	4.6	0.1	1.6	115%	2
Ni	60	40	43.8	0.5	1.2	110%	2
Cu	63	51.2	51.6	0.4	0.7	101%	2
Zn	66	313	303	8.1	2.7	97%	2
As	75	8	4.3	0.1	1.5	54%	2
Cd	111	2.2	2.5	0.005	0.2	114%	2
Sb	121	0.40	0.26	0.1	38	66%	2
Pb	208	63.8	64.0	2.4	3.8	100%	2